Electronic Supplementary Information (ESI) for *PCCP*

Experimental and theoretical study of enol-keto prototropic tautomerism and photophysics of azomethine-BODIPY dyads

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Electronic Supplementary Information (ESI):

Table S1-S8 & Fig. S1-S15 & Scheme S1

Table S1 Electrochemical data of **1** and **2**.[a]

Dyad	E_{ox}(vs SCE)/V		E_{red}(vs SCE)/V
	BODIPY$^{\bullet+}$/BODIPY	Azomethine$^{\bullet+}$	BODIPY/BODIPY$^{-\bullet}$
1	1.01	0.80	-1.69
2	1.04	0.62	-1.59

[a]$Ag/AgNO_3$ electrode was referenced after each series of experiments against the ferrocene/ferrocenium couple to obtain the potentials *vs* SCE.

Table S2 Summary of crystal data, intensity measurements and structure refinement for **1** and **2**.

Dyad	**1 (orange)**	**2 (red)**
Formula	$C_{26}H_{24}BF_2N_3O$	$C_{30}H_{26}BF_2N_3O$
Formula weight	443.29	493.35
T/K	173(2)	173(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a (Å)	10.2704(4)	9.2908(7)
b (Å)	10.7807(5)	10.8702(8)
c (Å)	11.5645(6)	13.9066(12)
α (deg)	73.4540(10)	102.090(7)
β (deg)	84.803(2)	94.075(7)
γ (deg)	62.6970(10)	114.538(7)
Z, D_{calcd}(g m^{-3})	2, 1.351	2, 1.333
V (Å^3)	1089.48(9)	1229.41(17)
μ (mm^{-1})	0.095	0.091
F (000)	464	516
T (K)	173(2)	173(2)
No. of reflns collected	9483	8504
No. of unique reflns.	4264 (R_{int} = 0.0263)	4842 (R_{int} = 0.0189)
No. of observed reflns	2834	3787
Parameters	307	342
R indices [I > 2σ(I)][a,b]	R_1 = 0.0408, wR_2 = 0.1139	R_1 = 0.0397, wR_2 = 0.0969
R indices (all data)	R_1 = 0.0749, wR_2 = 0.1688	R_1 = 0.0556, wR_2 = 0.1045
Goodness-of-fit on F^2	1.19	1.027
Largest diff. peak and hole (e Å^{-3})	0.27 and -0.32	0.20 and -0.22
CCDC number	1000809	1000810

[a]$R_1 = \Sigma| |F_o|-|F_c| | / \Sigma|F_o|$, [b]$wR_2 = [\Sigma w(F_o^2-F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$

Table S3 Selected molecular structure parameters for dyads **1** and **2**.

Dyad **1**					
Parameters	Experimental	B3LYP/6-31+G(d,p)	Parameters	Experimental	B3LYP/6-31+G(d,p)
Bond Lengths (Å)					
C1-C2	1.384(4)	1.405	C2-C3	1.378(3)	1.387
C3-C4	1.400(3)	1.411	C4-C5	1.408(4)	1.424
C5-C6	1.380(3)	1.403	C6-C1	1.388(4)	1.391
C5-O1	1.357(3)	1.344	C4-C7	1.447(3)	1.449
C7-N1	1.283(3)	1.294	C8-N1	1.421(3)	1.408
C8-C9	1.390(3)	1.406	C9-C10	1.390(3)	1.395
C10-C11	1.386(3)	1.401	C11-C12	1.389(3)	1.403
C12-C13	1.377(3)	1.393	C13-C8	1.392(3)	1.405
C11-C14	1.483(3)	1.495	B1-N2	1.553(3)	1.554
B1-N3	1.546(3)	1.554	B1-F1	1.391(3)	1.404
B1-F2	1.381(3)	1.405	N2-C19	1.354(3)	1.349
N2-C15	1.404(3)	1.402	N3-C21	1.353(3)	1.349
N3-C26	1.404(3)	1.402	O1-H1D	1.02(4)	0.996
Bond Angles (deg)					
C1-C2-C3	119.4(2)	119.09	C2-C3-C4	121.4(2)	121.31
C3-C4-C5	118.4(2)	118.85	C4-C5-C6	119.9(2)	119.56
C5-C6-C1	120.5(3)	120.13	O1-C5-C6	119.0(2)	118.67
O1-C5-C4	121.1(2)	121.77	C4-C7-N1	121.5(2)	122.45
C7-N1-C8	120.6(2)	121.11	C8-C9-C10	119.8(2)	120.34
C9-C10-C11	121.1(2)	120.88	C10-C11-C12	118.4(2)	118.67
C11-C12-C13	121.3(2)	120.75	C13-C8-C9	119.2(2)	118.78
F1-B1-F2	108.8(2)	109.68	N2-B1-N3	106.0(2)	106.86
F1-B1-N3	110.9(2)	110.09	F2-B1-N2	110.9(2)	110.04
Torsion Angles (deg)					
C7-N1-C8-C13	153.1(2)	145.06	C7-N1-C8-C9	-28.4(3)	-37.47
C10-C11-C14-C15	89.4(3)	90.00	C12-C11-C14-C15	-92.5(3)	-90.75
C5-C4-C7-N1	3.0(3)	-0.85	O1-C5-C4-C7	-1.6(4)	0.26
Dyad **2**					
Parameters	Experimental	B3LYP/6-31+G(d,p)	Parameters	Experimental	B3LYP/6-31+G(d,p)
Bond Lengths (Å)					
C1-C2	1.356(2)	1.379	C2-C3	1.405(2)	1.411
C3-C4	1.362(2)	1.383	C4-C5	1.407(2)	1.421
C5-C6	1.444(2)	1.449	C6-C7	1.404(2)	1.413
C7-C8	1.421(2)	1.420	C8-C9	1.349(2)	1.369
C9-C10	1.424(2)	1.427	C10-C5	1.424(2)	1.433
C7-O1	1.327(2)	1.337	C6-C11	1.438(2)	1.445
C11-N1	1.293(2)	1.300	C12-N1	1.415(2)	1.406
C12-C13	1.393(2)	1.407	C13-C14	1.382(2)	1.395
C14-C15	1.383(2)	1.401	C15-C16	1.388(2)	1.403

C16-C17	1.384(2)	1.393	C12-C17	1.387(2)	1.405
C15-C18	1.497(2)	1.495	B1-N2	1.539(2)	1.554
B1-N3	1.536(2)	1.554	B1-F1	1.379(2)	1.404
B1-F2	1.402(2)	1.405	N2-C19	1.400(2)	1.402
N2-C23	1.352(2)	1.349	N3-C25	1.347(2)	1.349
N3-C30	1.403(2)	1.402	O1-H1D	1.02(2)	1.007
		Bond Angles (deg)			
C1-C2-C3	119.0(2)	119.20	C2-C3-C4	120.9(2)	120.89
C3-C4-C5	121.7(1)	121.46	C4-C5-C10	117.2(1)	117.28
C5-C10-C1	120.5(3)	120.04	C2-C1-C10	121.6(1)	121.13
C10-C5-C6	119.0(1)	119.00	C5-C6-C7	119.4(1)	119.08
C7-C8-C9	120.7(1)	120.12	C8-C9-C10	121.8(1)	120.69
C1-C10-C9	121.5(1)	120.73	C1-C10-C5	119.5(1)	120.04
C9-C10-C5	118.9(1)	119.23	N1-C11-C6	121.8(1)	122.49
O1-C7-C6	122.3(1)	122.38	O1-C7-C8	117.6(1)	116.75
C13-C12-C17	118.5(1)	118.68	C12-C13-C14	120.0(1)	120.40
C13-C14-C15	121.6(1)	120.88	C14-C15-C16	118.4(1)	118.64
C15-C16-C17	120.3(1)	120.79	C16-C17-C12	121.2(1)	120.58
F1-B1-F2	108.8(1)	109.67	N2-B1-N3	107.3(1)	106.86
F1-B1-N3	111.0(1)	110.06	F2-B1-N2	109.0(1)	110.09
		Torsion Angles (deg)			
C11-N1-C12-C17	177.2(1)	146.11	C11-N1-C12-C13	-1.6(2)	-36.37
C14-C15-C18-C30	96.3(2)	91.91	C14-C15-C18-C19	-89.0(2)	-87.95
C7-C6-C11-N1	0.3(2)	-1.71	O1-C7-C6-C11	-1.4(2)	0.79

Table S4 Percentage contribution from individual intermolecular interactions to the Hirshfeld surface of **1** and **2**.

Dyad	H···F	H···H	C···C	H···C	O···H
1	5.2	51.7	1.9	10.4	3.0
2	3.7	52.4	2.6	11.5	2.7

Table S5 Cartesian coordinates for DFT optimized structure of **1** (*enol*).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.896609	0.149139	-0.307649
2	1	0	-9.980415	0.078953	-0.284477
3	6	0	-8.274977	1.035806	-1.203569
4	1	0	-8.870383	1.649717	-1.871131
5	6	0	-6.890220	1.115019	-1.222385
6	1	0	-6.391553	1.795563	-1.908662
7	6	0	-6.098525	0.323546	-0.362812
8	6	0	-6.744916	-0.567944	0.539843
9	6	0	-8.146191	-0.643108	0.554203
10	1	0	-8.618340	-1.329319	1.249429
11	6	0	-4.654522	0.429954	-0.413379
12	1	0	-4.240383	1.143526	-1.137771
13	6	0	-2.479138	-0.181597	0.244280
14	6	0	-1.817708	-0.066778	-0.991461
15	1	0	-2.389774	-0.052675	-1.914182
16	6	0	-0.425038	-0.015428	-1.042983
17	1	0	0.074638	0.064083	-2.004393
18	6	0	0.340996	-0.081054	0.128653
19	6	0	-0.320242	-0.213964	1.358372
20	1	0	0.260221	-0.275588	2.274486
21	6	0	-1.710663	-0.275943	1.416430
22	1	0	-2.219474	-0.385498	2.369137
23	6	0	1.833930	-0.026940	0.062126
24	6	0	2.481802	1.219097	0.126234
25	6	0	1.977156	2.556283	0.264416
26	6	0	0.561502	3.038948	0.392127
27	1	0	0.552575	4.130032	0.466005
28	1	0	0.067338	2.637114	1.282276
29	1	0	-0.052780	2.753207	-0.467220
30	6	0	3.092739	3.387975	0.265783
31	1	0	3.087891	4.466590	0.353273
32	6	0	4.248858	2.590340	0.132635
33	6	0	5.671795	3.041467	0.080881
34	1	0	6.254325	2.589318	0.889911
35	1	0	5.723601	4.128972	0.168995
36	1	0	6.142892	2.736927	-0.859279
37	6	0	4.418658	-2.454410	-0.268609
38	6	0	5.868564	-2.797086	-0.375186

39	1	0	6.413341	-2.467826	0.515623
40	1	0	6.326672	-2.293773	-1.232523
41	1	0	5.990978	-3.876598	-0.487986
42	6	0	3.318881	-3.338460	-0.273430
43	1	0	3.386605	-4.415239	-0.357228
44	6	0	2.150045	-2.593845	-0.151627
45	6	0	0.770640	-3.184695	-0.115218
46	1	0	0.835748	-4.271444	-0.217881
47	1	0	0.136123	-2.806668	-0.922580
48	1	0	0.252218	-2.965668	0.823458
49	6	0	2.563668	-1.220578	-0.070715
50	7	0	-3.879846	-0.259137	0.361068
51	7	0	3.879844	1.295549	0.050979
52	7	0	3.963709	-1.190620	-0.147111
53	8	0	-6.048969	-1.344878	1.386726
54	1	0	-5.081231	-1.155964	1.244396
55	5	0	4.844688	0.088475	-0.110127
56	9	0	5.731888	0.031972	0.977095
57	9	0	5.570180	0.208461	-1.307224

Table S6 Cartesian coordinates for DFT optimized structure of **1** (*keto*).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.922347	-0.005091	-0.045316
2	6	0	-8.431501	0.164037	-1.377590
3	6	0	-7.079770	0.195769	-1.595622
4	6	0	-6.155117	0.061931	-0.511384
5	6	0	-6.647076	-0.110059	0.863135
6	6	0	-8.080043	-0.136480	1.029238
7	6	0	-4.779664	0.096317	-0.758736
8	6	0	-2.478919	-0.013464	0.118749
9	6	0	-1.791424	0.026002	-1.104512
10	6	0	-0.397747	0.031941	-1.119810
11	6	0	0.342567	-0.006112	0.069626
12	6	0	-0.351768	-0.050650	1.286520
13	6	0	-1.743709	-0.054010	1.314743
14	6	0	1.837368	-0.001957	0.035215
15	6	0	2.523271	1.224753	0.037850
16	6	0	2.059758	2.583543	0.084401
17	6	0	0.658339	3.117541	0.150469
18	6	0	3.201580	3.377840	0.062591

19	6	0	4.333767	2.537409	0.004774
20	6	0	5.771385	2.939941	-0.037551
21	6	0	4.346488	-2.525886	-0.085559
22	6	0	5.786228	-2.919486	-0.138000
23	6	0	3.218341	-3.373504	-0.064519
24	6	0	2.072479	-2.586342	-0.016070
25	6	0	0.673503	-3.129442	0.020390
26	6	0	2.529343	-1.224422	-0.006708
27	7	0	-3.879135	-0.021243	0.218087
28	7	0	3.924364	1.252404	-0.008857
29	7	0	3.930723	-1.243352	-0.050701
30	8	0	-5.850225	-0.227117	1.844193
31	5	0	4.852408	0.007537	-0.069817
32	9	0	5.710214	-0.008744	1.041733
33	9	0	5.610041	0.029114	-1.252489
34	1	0	-9.997488	-0.029299	0.115657
35	1	0	-9.129183	0.265048	-2.202224
36	1	0	-6.686553	0.322844	-2.602480
37	1	0	-8.457589	-0.264033	2.038699
38	1	0	-4.421104	0.227422	-1.776976
39	1	0	-2.326550	0.045126	-2.047556
40	1	0	0.123258	0.061899	-2.072368
41	1	0	0.201715	-0.082026	2.220420
42	1	0	-2.270163	-0.085906	2.264335
43	1	0	0.684402	4.210406	0.177158
44	1	0	0.126175	2.771818	1.042114
45	1	0	0.058427	2.815915	-0.713748
46	1	0	3.230401	4.459335	0.086544
47	1	0	6.318079	2.523767	0.814701
48	1	0	5.856353	4.028681	-0.018258
49	1	0	6.255906	2.560018	-0.942804
50	1	0	6.326263	-2.539254	0.735097
51	1	0	6.273774	-2.497203	-1.022566
52	1	0	5.876420	-4.007596	-0.166555
53	1	0	3.252481	-4.454950	-0.082837
54	1	0	0.704269	-4.221878	-0.016338
55	1	0	0.071179	-2.780610	-0.824102
56	1	0	0.141062	-2.838645	0.931279
57	1	0	-4.357722	-0.130334	1.147532

Table S7 Cartesian coordinates for DFT optimized structure of **2** (*enol*).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.619690	0.988260	0.937890
2	1	0	9.669579	0.736298	0.811665
3	6	0	8.248588	2.064404	1.716812
4	1	0	8.999058	2.671894	2.212919
5	6	0	6.878343	2.370092	1.860969
6	1	0	6.576477	3.217733	2.469491
7	6	0	5.910747	1.605793	1.235242
8	1	0	4.872386	1.884593	1.372345
9	6	0	6.255694	0.487839	0.428604
10	6	0	5.282595	-0.348806	-0.245133
11	6	0	5.735702	-1.428967	-1.035884
12	6	0	7.122558	-1.705694	-1.165377
13	1	0	7.416083	-2.548283	-1.782253
14	6	0	8.042514	-0.921463	-0.522790
15	1	0	9.102936	-1.137888	-0.623862
16	6	0	7.649024	0.186987	0.284458
17	6	0	3.863466	-0.108490	-0.122147
18	1	0	3.534869	0.721854	0.507590
19	6	0	1.600765	-0.619899	-0.541263
20	6	0	1.048658	-0.260642	0.701763
21	1	0	1.690921	-0.154978	1.570788
22	6	0	-0.328045	-0.084390	0.838128
23	1	0	-0.741691	0.183906	1.806301
24	6	0	-1.187979	-0.265434	-0.253338
25	6	0	-0.637687	-0.641995	-1.487501
26	1	0	-1.292137	-0.795066	-2.340959
27	6	0	0.735244	-0.828637	-1.628620
28	1	0	1.156855	-1.124887	-2.584160
29	6	0	-2.663141	-0.075986	-0.099986
30	6	0	-3.226570	1.185346	-0.360860
31	6	0	-2.641583	2.429162	-0.776201
32	6	0	-1.208389	2.763669	-1.071560
33	1	0	-1.127280	3.821155	-1.338318
34	1	0	-0.809839	2.174688	-1.903574
35	1	0	-0.555813	2.580211	-0.212452
36	6	0	-3.693796	3.335150	-0.867432
37	1	0	-3.620608	4.375346	-1.156826
38	6	0	-4.889606	2.672477	-0.519036

39	6	0	-6.270287	3.240344	-0.471986
40	1	0	-6.940029	2.693879	-1.143691
41	1	0	-6.252509	4.292477	-0.764966
42	1	0	-6.692371	3.157714	0.534833
43	6	0	-5.375746	-2.178067	0.852085
44	6	0	-6.832944	-2.374765	1.114562
45	1	0	-7.188449	-1.680693	1.882632
46	1	0	-7.018801	-3.398987	1.445599
47	1	0	-7.422013	-2.180296	0.212246
48	6	0	-4.342706	-3.133909	0.953933
49	1	0	-4.477794	-4.167098	1.246059
50	6	0	-3.138476	-2.523892	0.617408
51	6	0	-1.809906	-3.222400	0.604405
52	1	0	-1.947104	-4.274534	0.869031
53	1	0	-1.105471	-2.784437	1.318503
54	1	0	-1.330534	-3.180524	-0.378250
55	6	0	-3.461186	-1.159544	0.304800
56	5	0	-5.638074	0.314603	0.225444
57	7	0	2.976765	-0.831000	-0.739858
58	7	0	-4.606354	1.388699	-0.217228
59	7	0	-4.845540	-1.000410	0.463377
60	9	0	-6.597129	0.123449	-0.782564
61	9	0	-6.273047	0.716792	1.412257
62	8	0	4.897055	-2.236075	-1.693504
63	1	0	3.961464	-1.910953	-1.512839

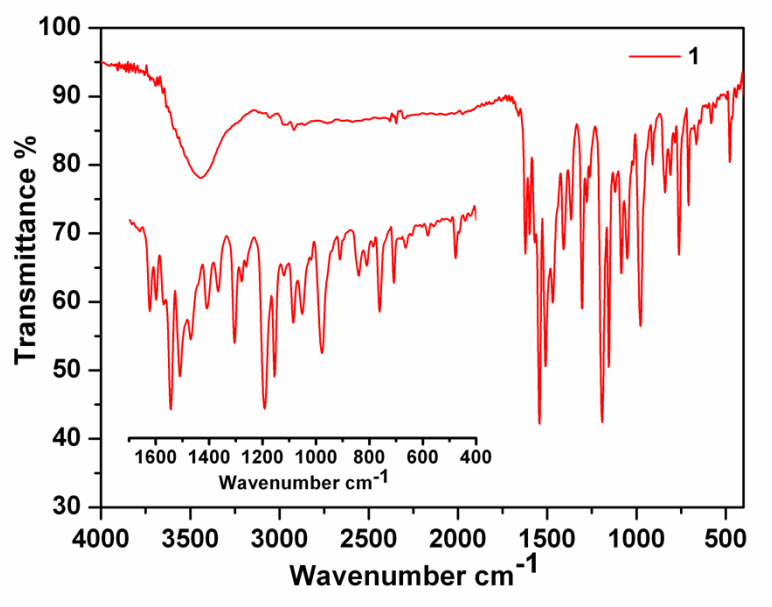
Table S8 Cartesian coordinates for DFT optimized structure of **2** (*keto*).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.767808	-0.000082	1.193429
2	6	0	-8.491786	-0.000576	2.551520
3	6	0	-7.152377	-0.000887	2.973624
4	6	0	-6.117755	-0.000694	2.047236
5	6	0	-6.368431	-0.000171	0.656307
6	6	0	-5.315467	0.000038	-0.364065
7	6	0	-5.668052	0.000668	-1.788586
8	6	0	-7.079488	0.000785	-2.131710
9	6	0	-8.039511	0.000575	-1.172512
10	6	0	-7.730410	0.000123	0.237103
11	6	0	-3.969018	-0.000209	-0.010115
12	6	0	-1.588916	-0.000266	-0.651609

13	6	0	-1.033938	-0.001391	0.638663
14	6	0	0.350058	-0.001355	0.803464
15	6	0	1.214334	-0.000271	-0.299219
16	6	0	0.653685	0.000770	-1.583987
17	6	0	-0.726956	0.000771	-1.761651
18	6	0	2.696880	-0.000133	-0.105460
19	6	0	3.380755	-1.224625	-0.013618
20	6	0	2.925310	-2.585192	-0.080237
21	6	0	1.538062	-3.123961	-0.276992
22	6	0	4.059297	-3.376077	0.074625
23	6	0	5.178969	-2.531753	0.232215
24	6	0	6.605217	-2.929397	0.427756
25	6	0	5.178202	2.532133	0.232944
26	6	0	6.604328	2.930167	0.428579
27	6	0	4.058240	3.376156	0.075783
28	6	0	2.924502	2.584962	-0.079318
29	6	0	1.537045	3.123328	-0.275709
30	6	0	3.380396	1.224526	-0.013271
31	5	0	5.685417	0.000252	0.314213
32	7	0	-2.968708	-0.000107	-0.902185
33	7	0	4.769632	-1.247762	0.178274
34	7	0	4.769277	1.248030	0.178524
35	9	0	6.654005	0.000486	-0.702289
36	9	0	6.316322	0.000223	1.569317
37	8	0	-4.793172	0.000693	-2.700099
38	1	0	-9.797281	0.000145	0.843971
39	1	0	-9.297613	-0.000733	3.278759
40	1	0	-6.917809	-0.001290	4.034245
41	1	0	-5.100594	-0.000966	2.424545
42	1	0	-7.321447	0.001108	-3.189506
43	1	0	-9.089497	0.000748	-1.457765
44	1	0	-3.681422	-0.000431	1.034590
45	1	0	-1.664442	-0.002330	1.520870
46	1	0	0.765136	-0.002204	1.807207
47	1	0	1.304294	0.001627	-2.453689
48	1	0	-1.146449	0.001628	-2.763683
49	1	0	1.566851	-4.217096	-0.276061
50	1	0	1.099383	-2.799499	-1.225649
51	1	0	0.853285	-2.804259	0.514630
52	1	0	4.090819	-4.457759	0.075211
53	1	0	7.231982	-2.542311	-0.382186
54	1	0	6.690641	-4.017974	0.454494
55	1	0	7.000795	-2.516794	1.361350
56	1	0	6.999942	2.517697	1.362220

57	1	0	6.689449	4.018768	0.455311
58	1	0	7.231265	2.543234	-0.381299
59	1	0	4.089407	4.457848	0.076820
60	1	0	1.565307	4.216475	-0.273327
61	1	0	0.852212	2.802230	0.515294
62	1	0	1.098780	2.799923	-1.224925
63	1	0	-3.331251	0.000123	-1.878382

(a)



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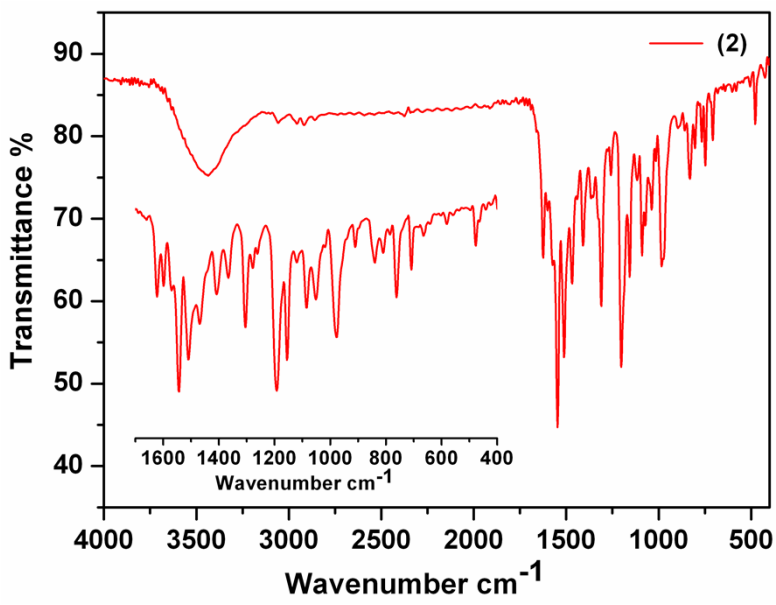
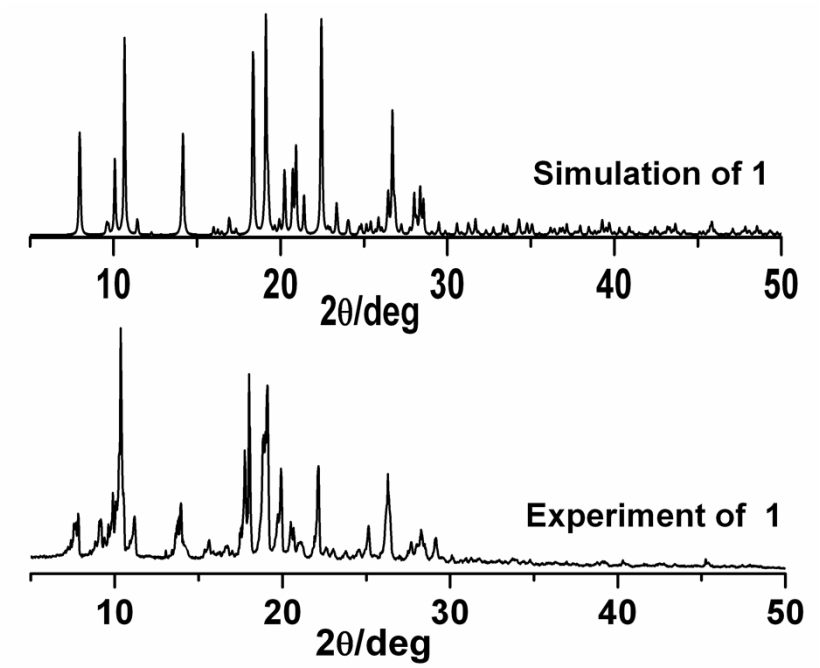


Fig. S1 Solid-state FT-IR spectra of **1** (a) and **2** (b).

(a)



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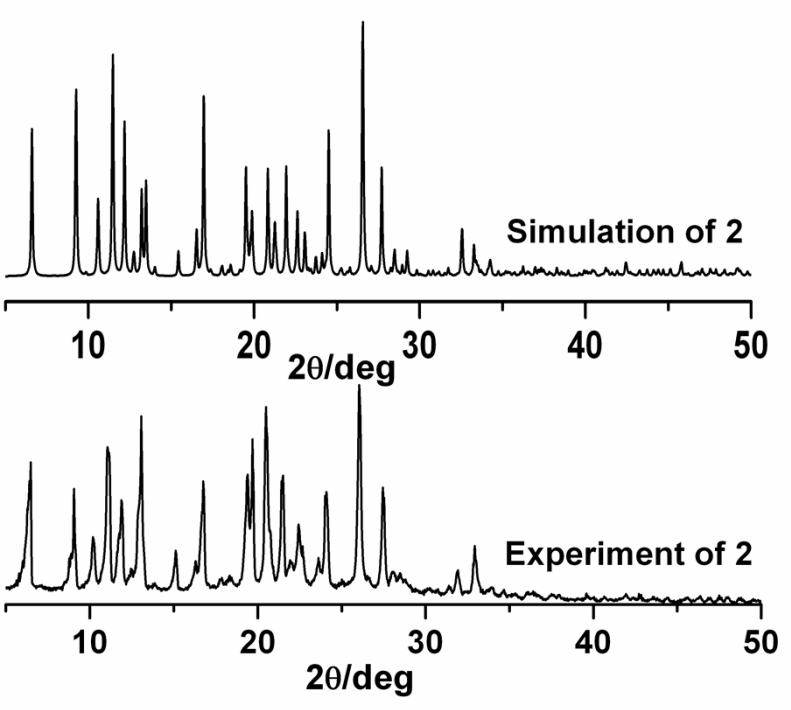
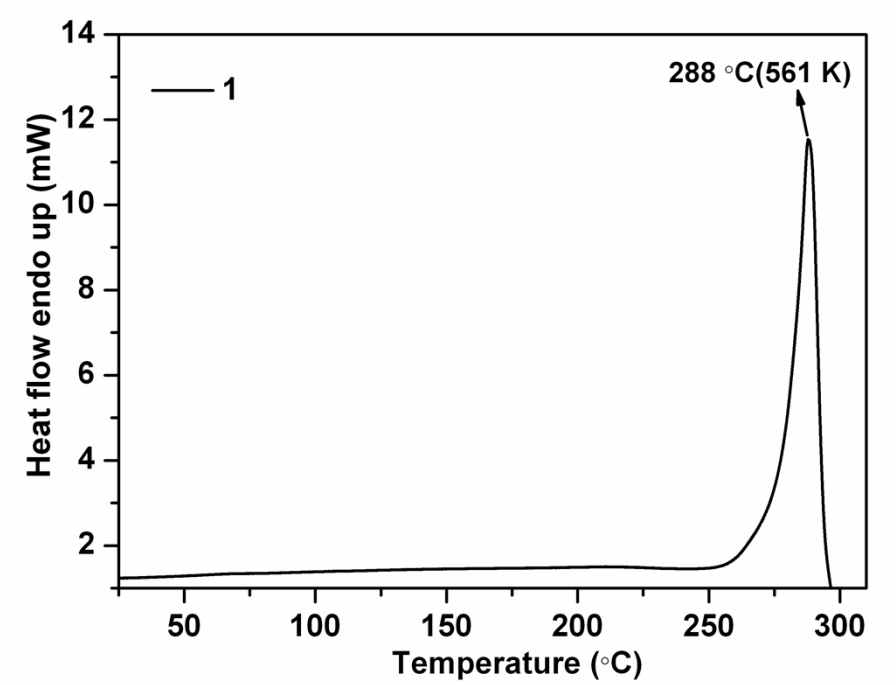


Fig. S2 Comparison between the calculated powder X-ray diffractions and the experimental powder X-ray diffractions of **1** (a) and **2** (b) at room temperature.

(a)



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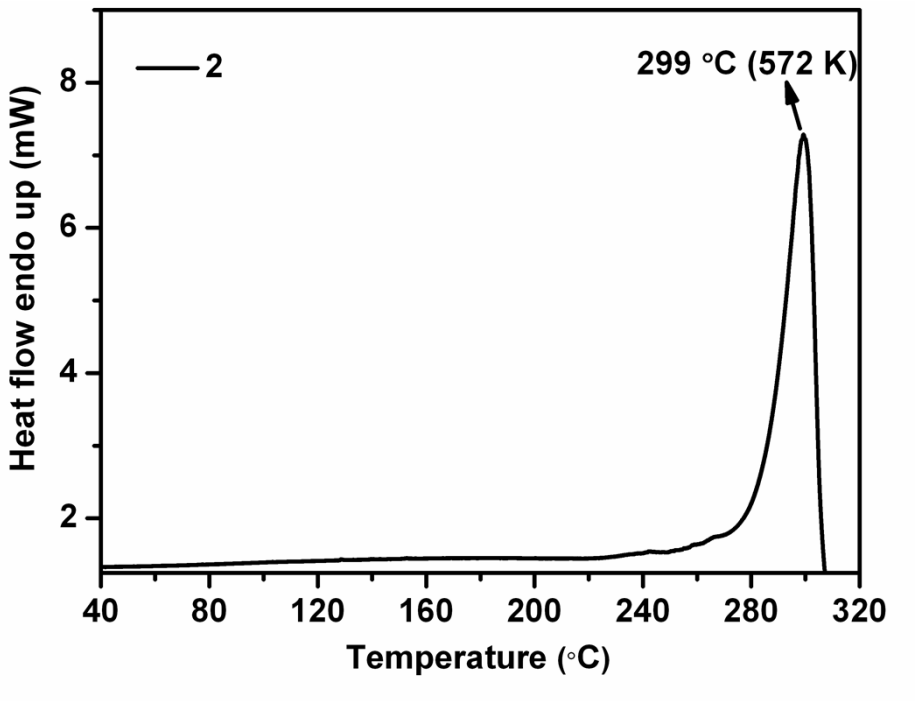
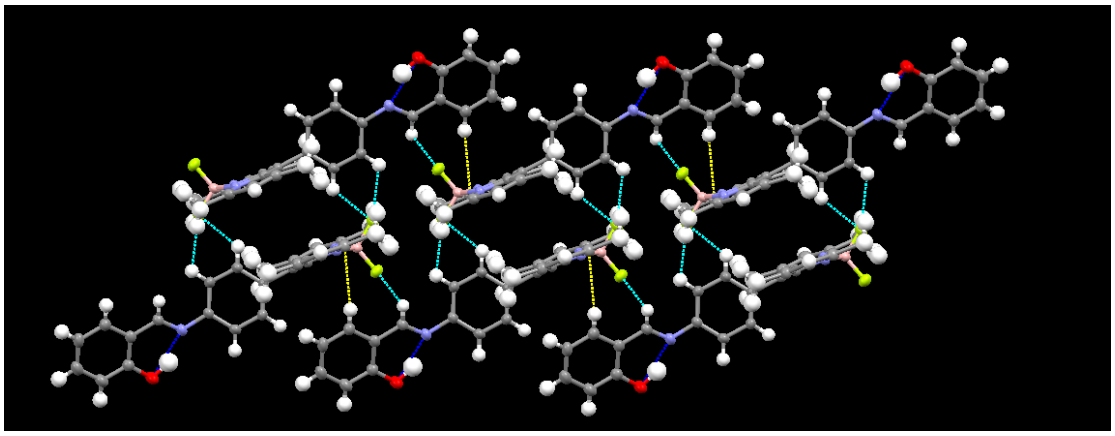


Fig. S3 Differential scanning calorimetric (DSC) plots of **1**(a) and **2**(b).

(a)



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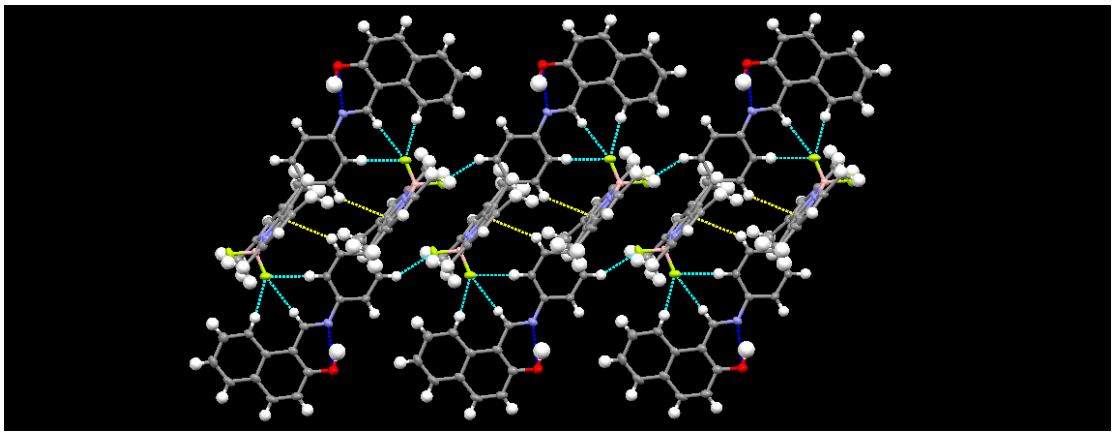
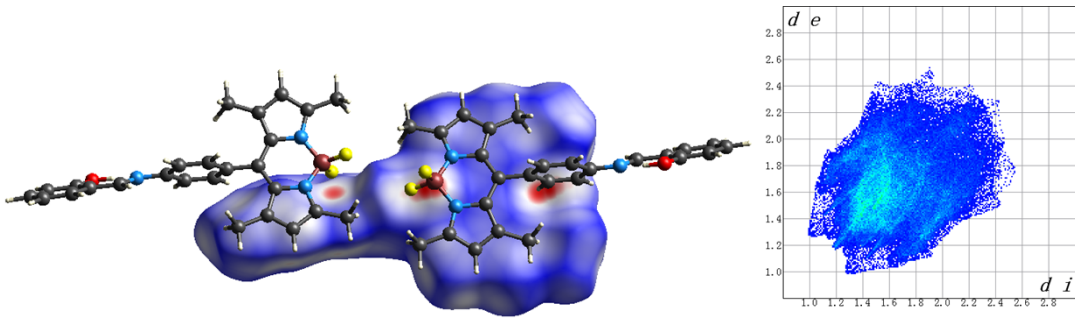


Fig. S4 The intermolecular interactions in crystals of **1**(a) and **2**(b).

(a)



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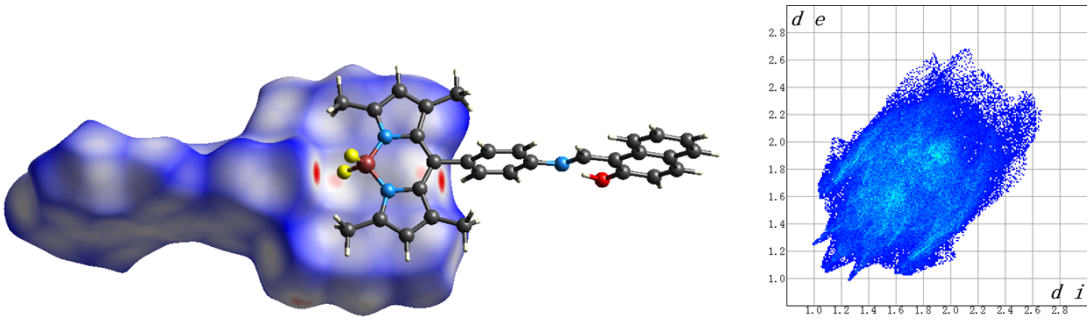


Fig. S5 Crystal packing for (a) **1** and (b) **2**, showing the Hirshfeld surfaces of the central molecules mapped with d_{norm} (left) and the 2D fingerprint plots showing the distribution of the d_e distances as a function of d_i (right).

Hirshfeld surface analyses for 1 and 2

Molecular Hirshfeld surfaces in the crystal structure and the associated 2D-fingerprint plots were calculated using *CrystalExplorer* 3.0 program,[1] which accepts a structure input file in CIF format. Bond lengths to hydrogen atoms were set to typical neutron values (C-H = 1.083 Å, N-H = 1.009 Å).[2] For each point on that isosurface two distances are defined: d_e, the distance from the point to the nearest nucleus external to the surface, and d_i, the distance to the nearest nucleus internal to the surface. The normalized contact distance (d_{norm})[1a] based on d_e and d_i is given by:

$$d_{norm} = (d_i - r_i^{vdw})/r_i^{vdw} + (d_e - r_e^{vdw})/r_e^{vdw}$$

Where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on whether the intermolecular contacts are shorter or longer than the van der Waals separations. The parameter d_{norm} defines a surface with a red-white-blue color scheme, where red highlights shorter contacts, white is used for contacts around the van der Waals

separation, and blue is for longer contacts. Hirshfeld surface fingerprint plots were generated using d_i and d_e as a pair of coordinates, in intervals of 0.01 Å, for each individual surface spot resulting in two-dimensional histograms.

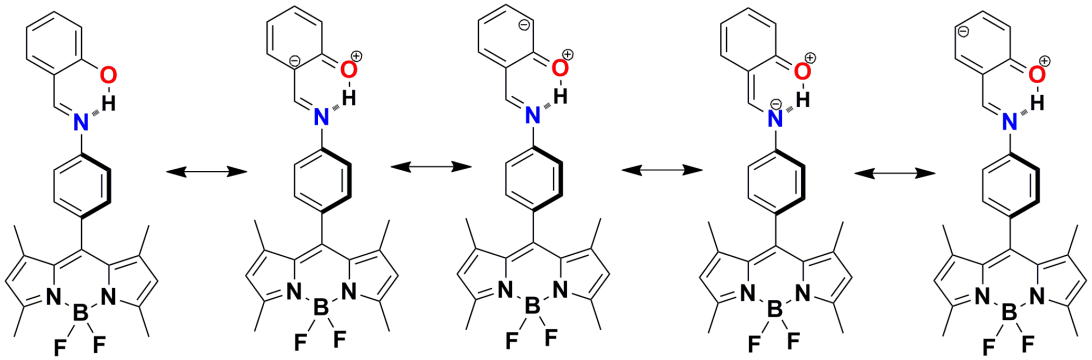
Comments: Hirshfeld surface calculations and relevant 2D fingerprint plots provide additional insight into the molecular interactions in these dyads **1** and **2**. For the visualization, we have used a mapping of the normalized contact distance, d_{norm}. Its negative value enables identification of molecular regions of great importance for intermolecular interactions. These F- and C-based interactions represent the closest contacts in the structure and can be viewed as a pair of red spots on the d_{norm} surface (Fig. S5 and Table S4 of ESI†).

References:

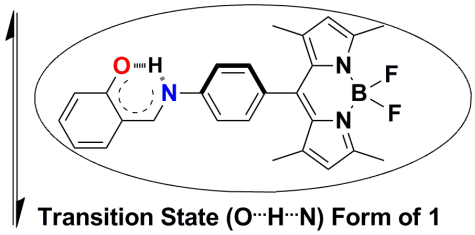
(1) (a) M. A. Spackman, J. J. Mckinnon, *CrystEngComm* 2002, **4**, 378-392; (b) M. Spackman, D. Jayatilaka, *CrystEngComm* 2009, **11**, 19-32; (c) M. A. Spackman, J. J. Mckinnon, D. Jayatilaka, *CrystEngComm*., 2008, **10**, 377-388.

(2) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perdin Trans. 2* 1987, S1-S19.

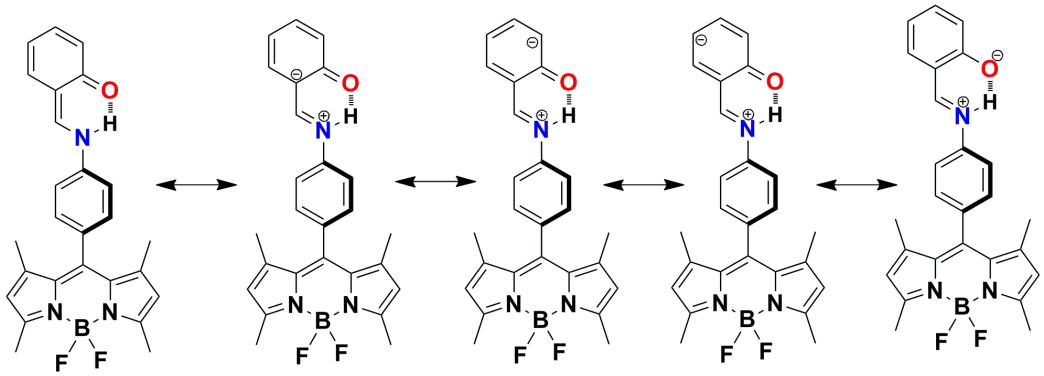
(a)



Resonant structures of molecular (OH) Form of 1



Transition State (O···H···N) Form of 1



Resonant structures of proton Transfer (NH) Form of 1

(b)

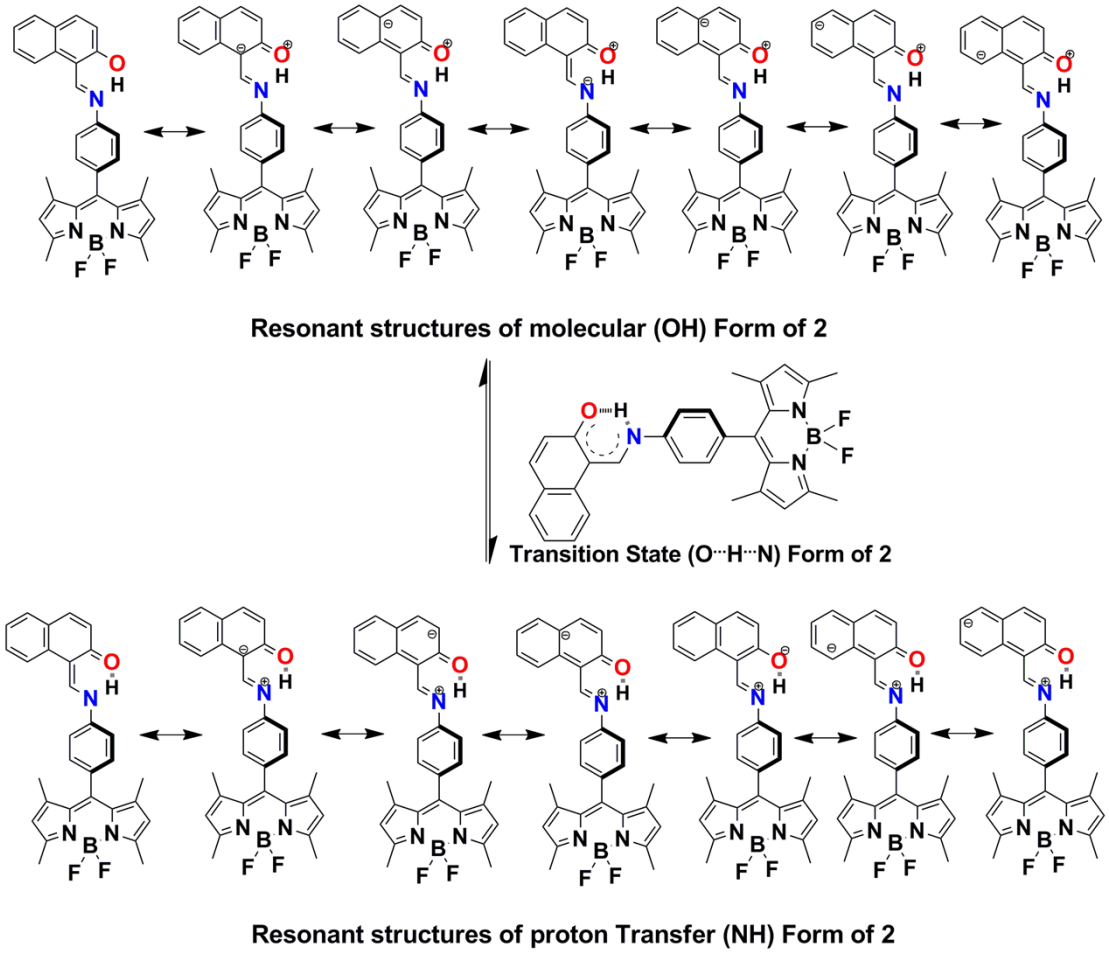


Fig. S6 The resonant structures of *enol-imine* and *keto-enamine* states for **1** (a) and **2**(b).

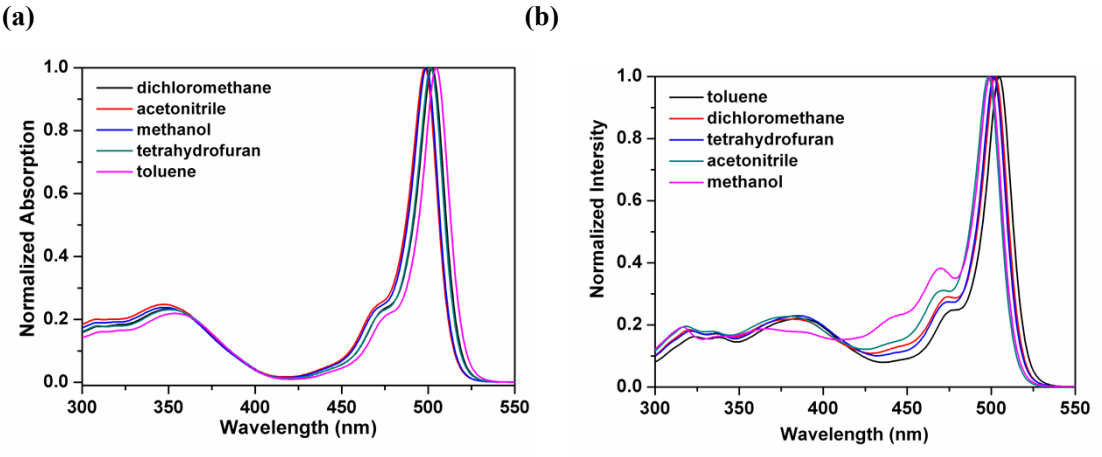


Fig. S7 Absorption spectra of **1** (a) and **2** (b) in several solvents.

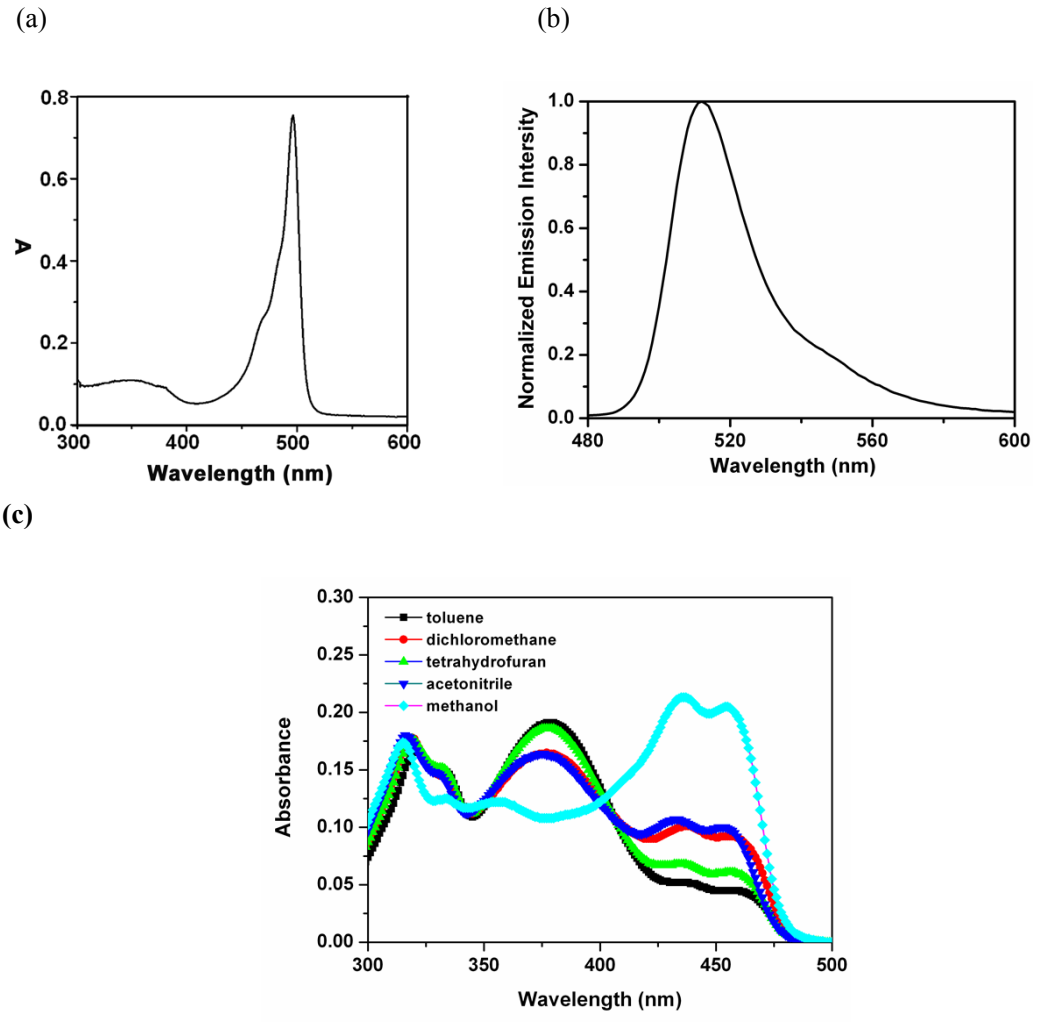


Fig. S8 Absorption (a) and emission spectrum (b) of the model **TM-BODIPY** in methanol; and absorption spectra (c) of **NA** in different solvents.

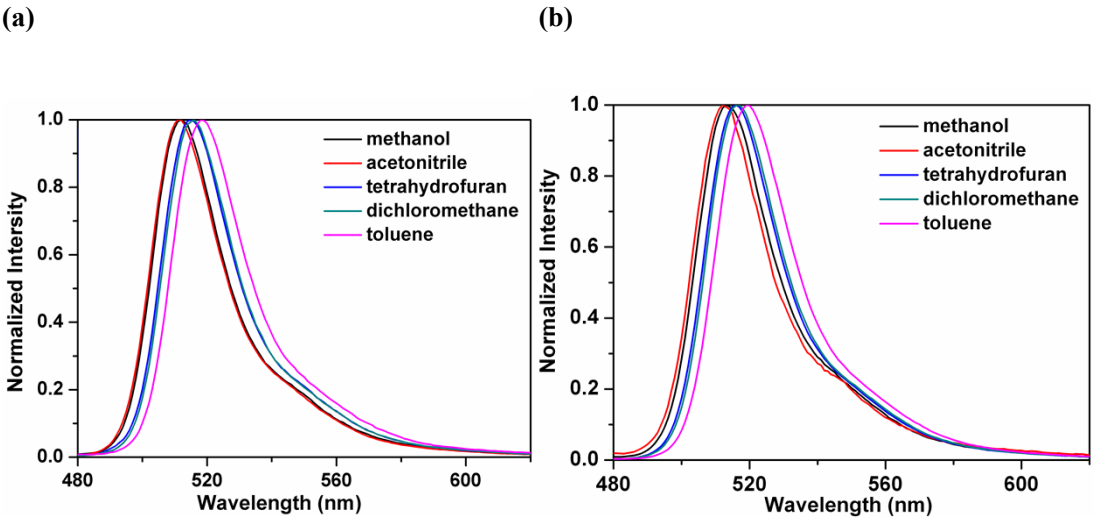


Fig S9 Fluorescence emission spectra of **1** (a) and **2** (b) in several solvents. All intensities have been normalized to the same value at the wavelength of maximum intensity.

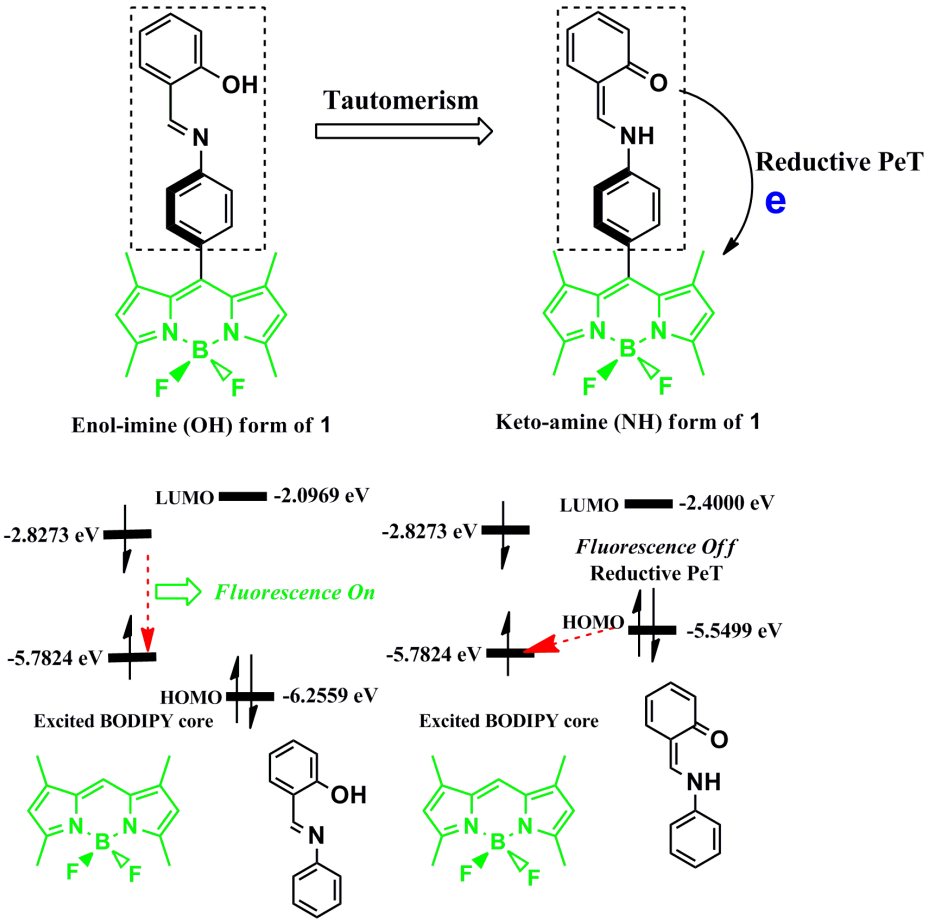


Fig S10 Proposed photoinduced electron transfer (PeT) mechanism between BODIPY moiety and *keto* unit of **1**.

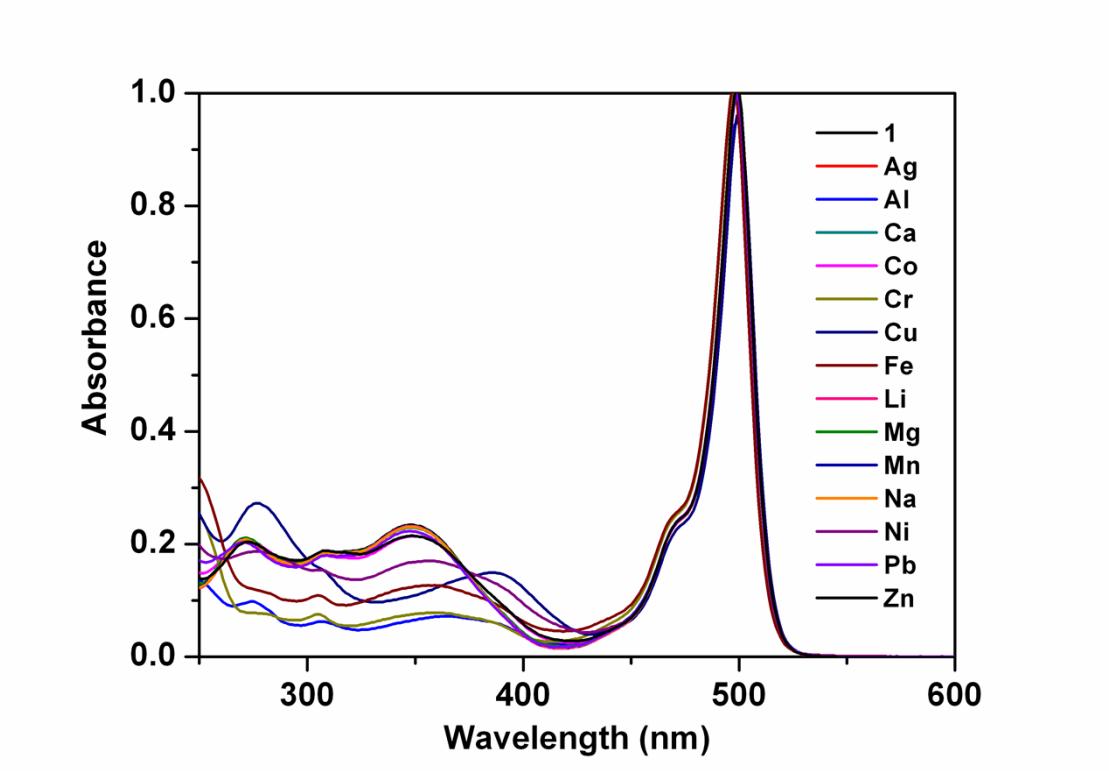


Fig. S11 Absorbance spectra of **1** (1.0×10^{-5} M) in the solution of MeOH/$CHCl_3$ (20:1, v/v) upon addition of 3 equiv of different metal ions.

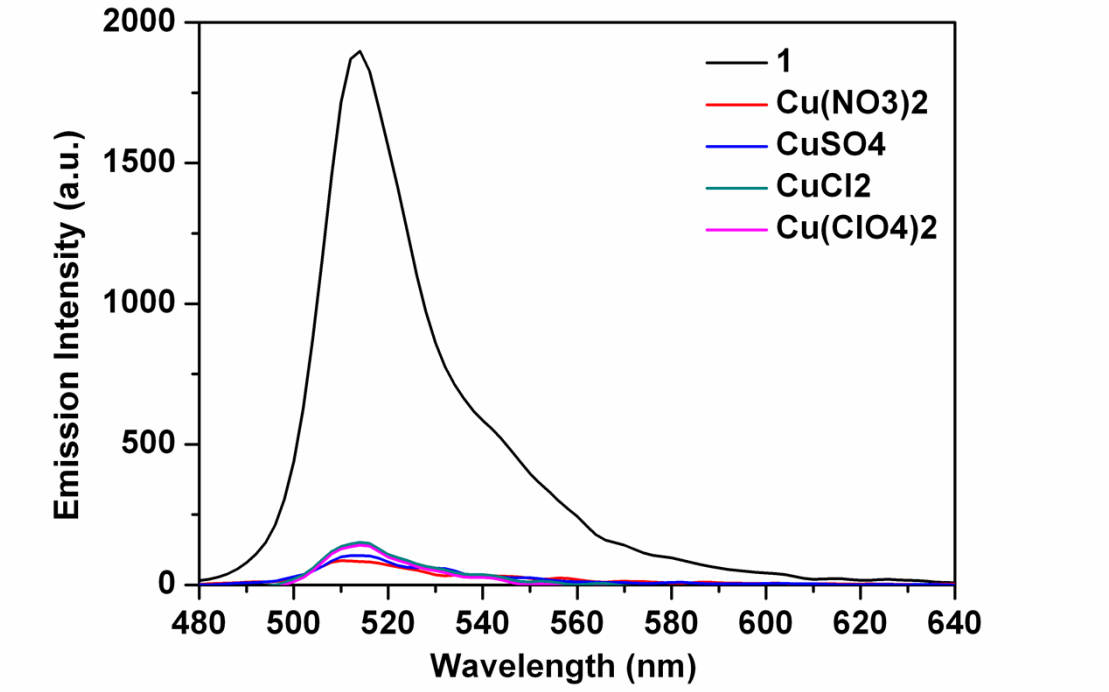
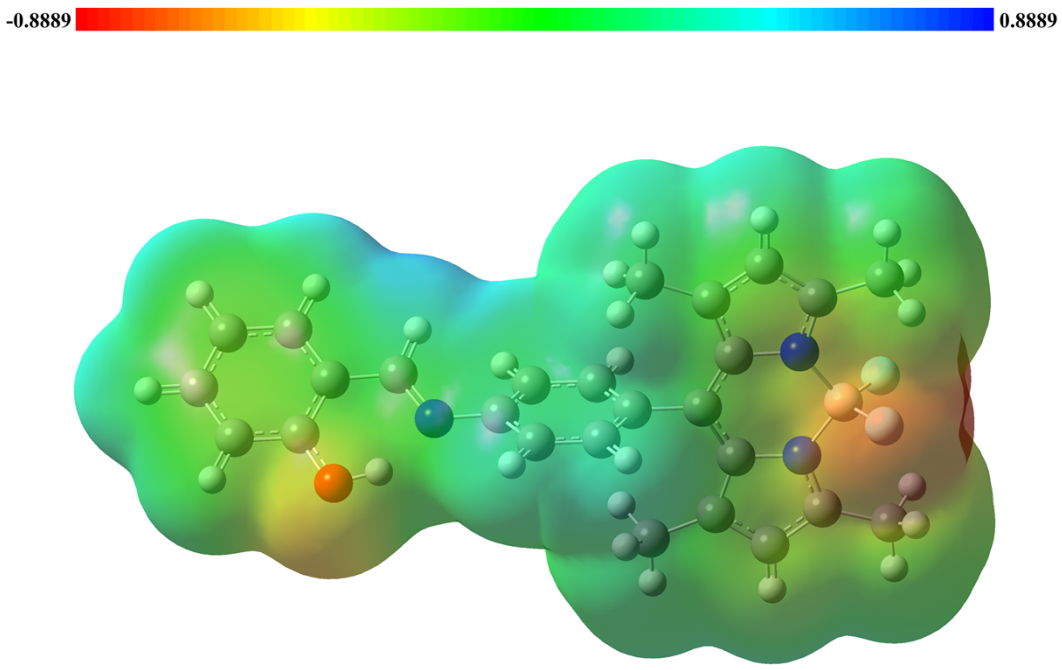
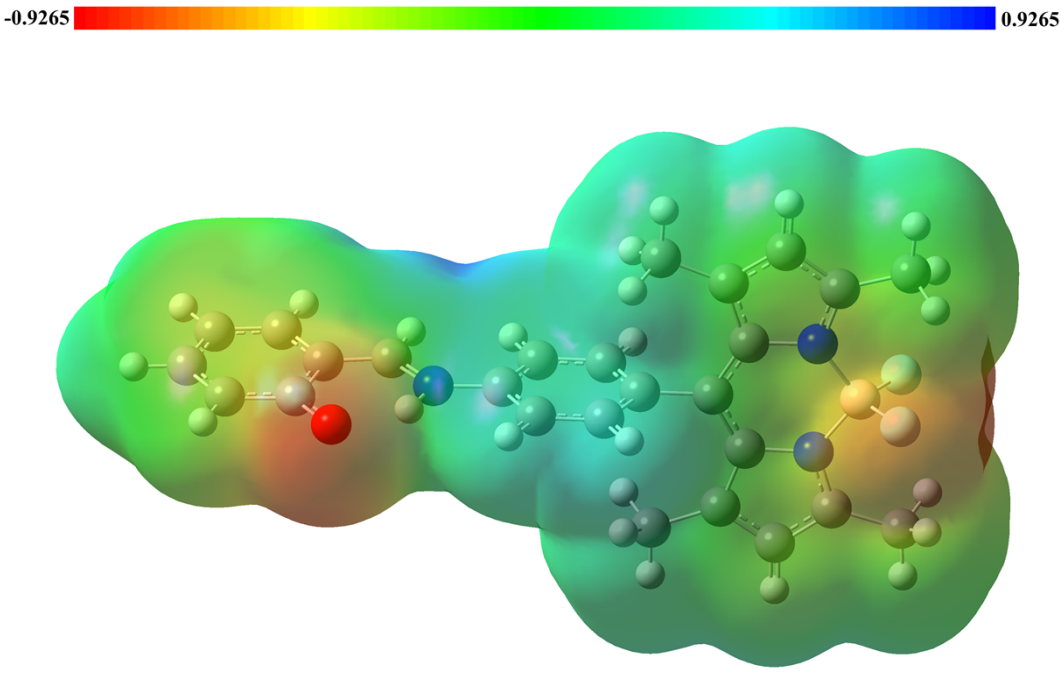


Fig. S12 Emission spectra of **1** (1.0×10^{-5} M) in the solution of MeOH/$CHCl_3$ (20:1, v/v) upon addition of 3 equiv of different copper salts.

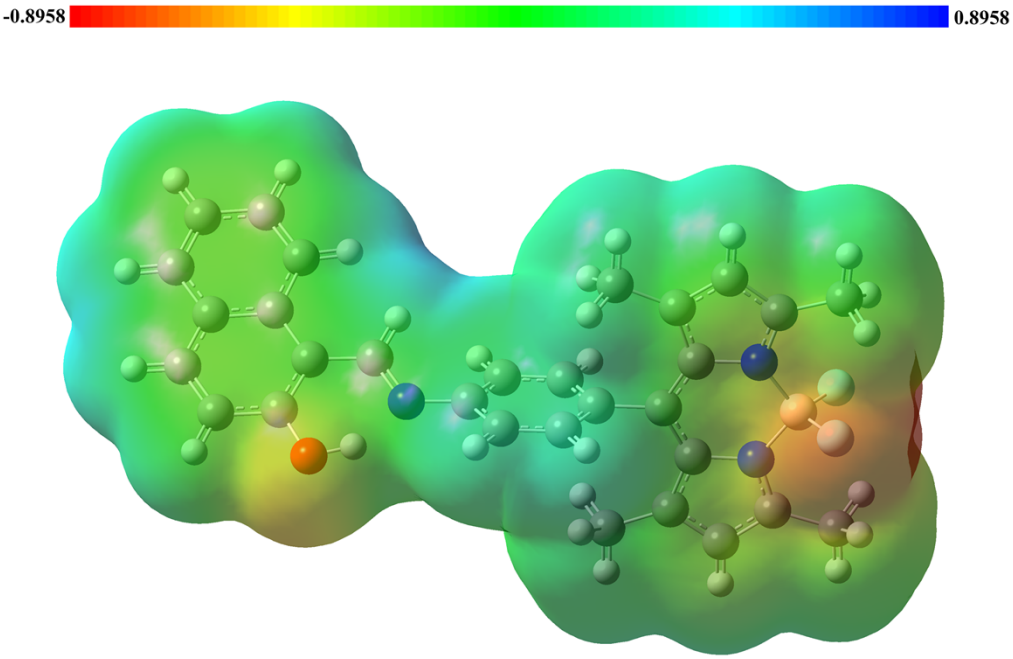
(a)



(b)



(c)



(d)

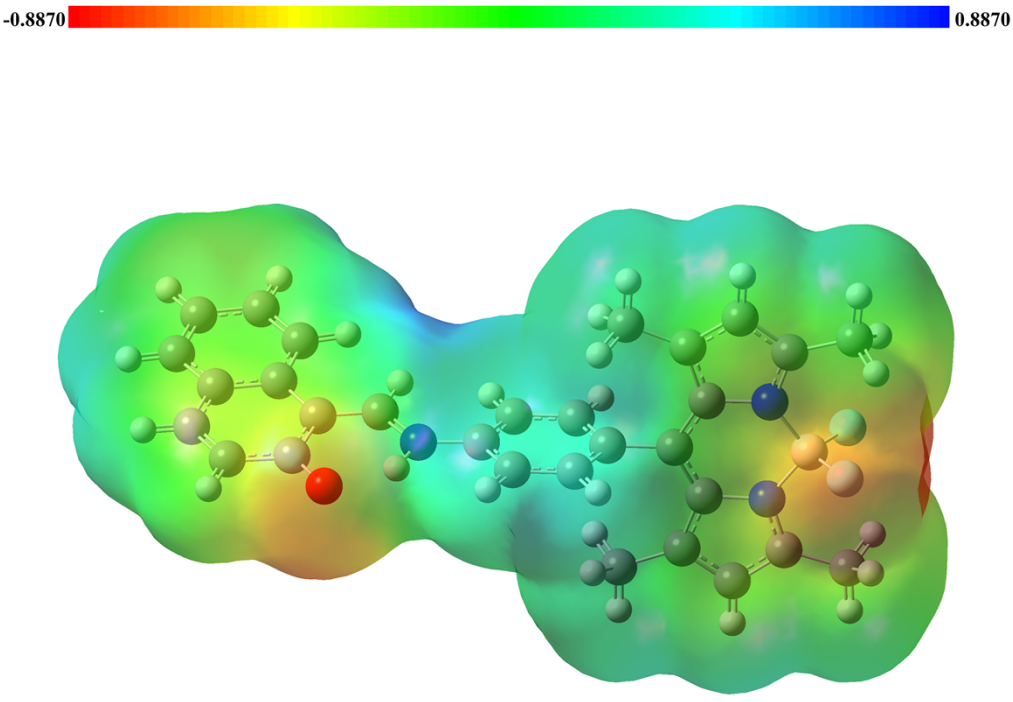


Fig. S13 Electrostatic potential maps of **1**-*enol* (a), **1**-*keto* (b), **2**-*enol* (c) and **2**-*keto* (d). Red = lowest potential (electron-rich) and blue = highest potential (electron-poor). Calculated with *Gaussian 09* (B3LYP/6-31+G(d,p) for C, N, O, B, F, H).

Comments: 3D plots of molecular electrostatic potential (MEP) of **1** and **2** are illustrated (Fig. S6 of ESI†). The MEP is a very useful descriptor for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions.[4] Different values of the electrostatic potential at the surface are represented by different colours. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. As can be seen from the MEP maps of **1** and **2**, negative regions are found around the phenol O1 atom for **1**, naphthol O1 atom for **2** and fluor atoms from BODIPY moieties. Regions having the positive potential are localized on the C7-H7A bond for **1** and C11-H11A bond for **2**, indicating possible sites for nucleophilic attack. According to these calculated results, the MEP map shows that the negative potential sites are on electronegative as well as the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have noncovalent interactions. In addition, the MEP is also best suited for identifying sites for intra- and intermolecular interactions.[5] When an intramolecular interaction takes place the electrostatic potential of the negative atom becomes less negative and the postitive region region on the other atom becomes less positive.[6] For the MEP surfaces in **1** and **2**, the weak negative regions associated with the N1 atom and also the weak positive region by the nearby H1D for **1** or H1B for **2** atom are indicative of intramolecular O1-H1D···N1 and O1-H1B···N1 hydrogen bondings.

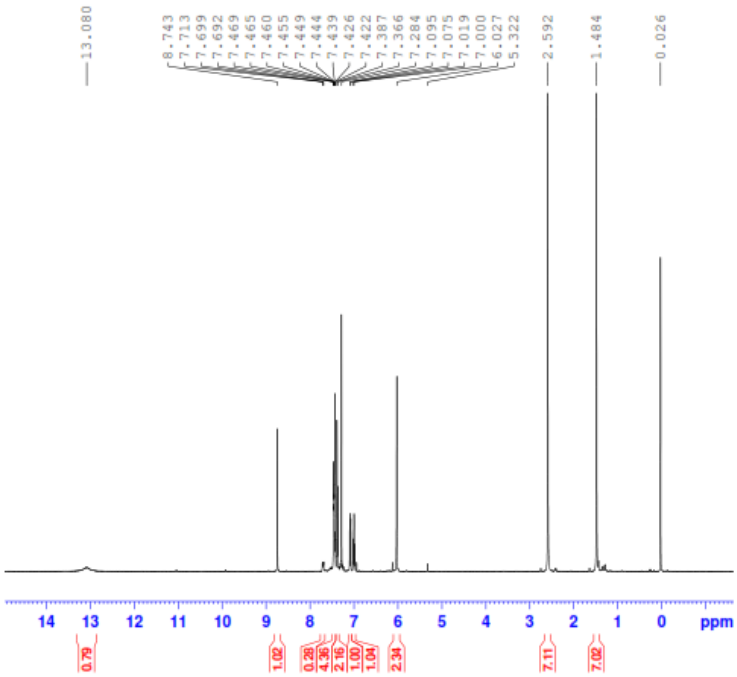
References:

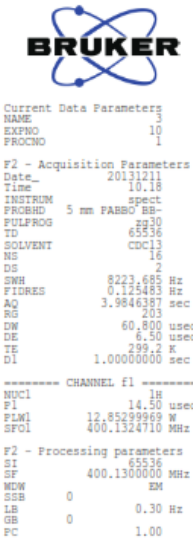
(4) N. Okulik, A. H. Jubert, *Internet Electron. J. Mol. Des*., 2005, **4**, 17-30.

(5) P. Politzer, M. C. Concha, J. S. Murray, *Int. J. Quantum Chem*., 2000, **80**, 184-192.

(6) W. Hussein, C. G. Walker, Z. Peralta-Inga, J. S. Murray, *Int. J. Quantum Chem*., 2001, **82**, 160-169.

(a)





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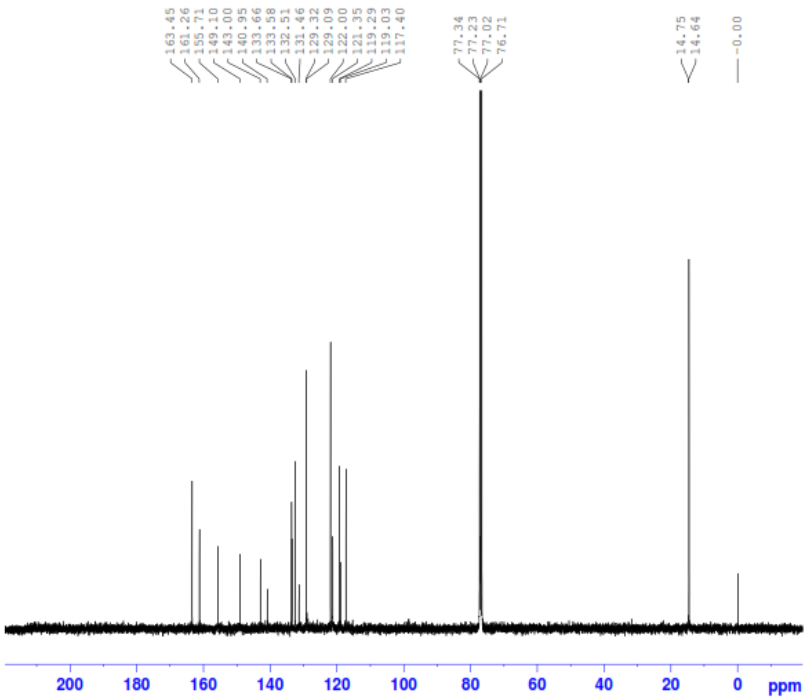


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Fig. S14 (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **1**.

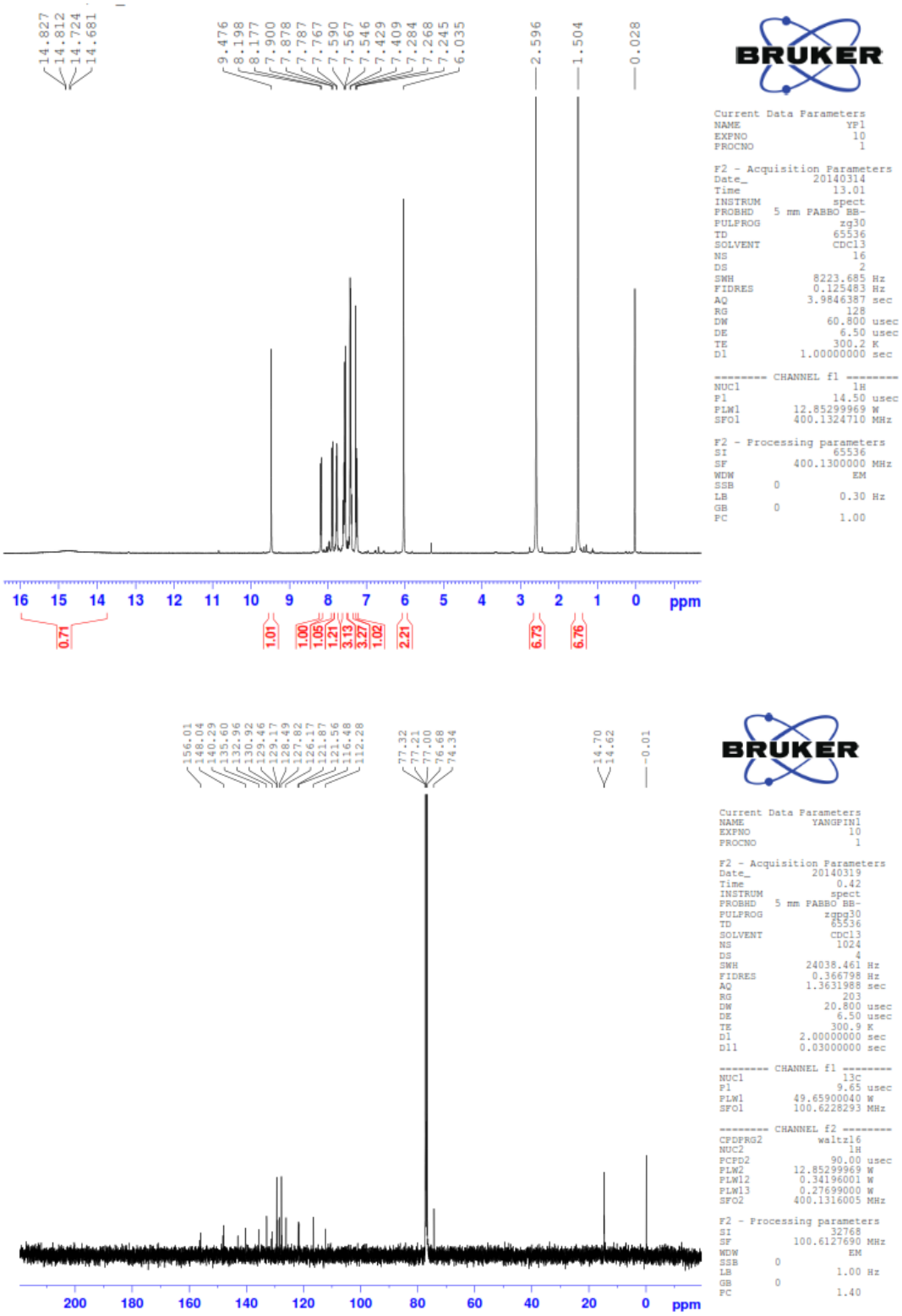
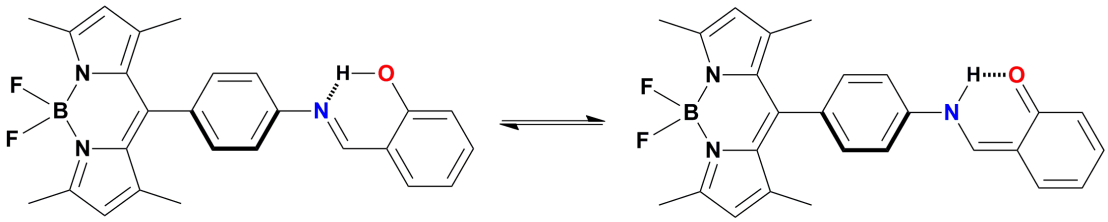


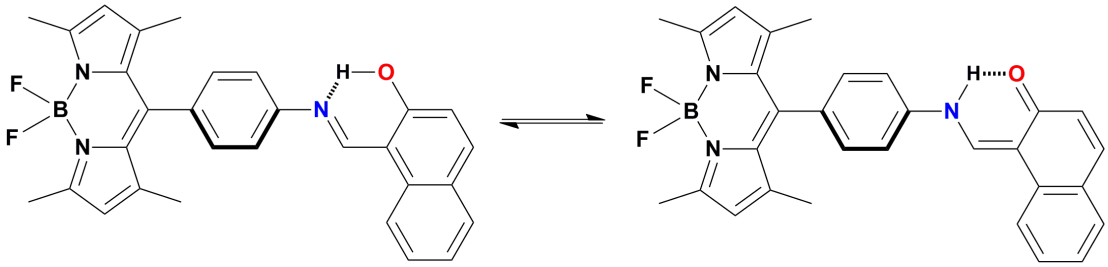
Fig. S15 (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **2**.

(a)



Enol-imine **(OH) form of 1** ***Keto-enamine*** **(NH) form of 1**

(b)



Enol-imine **(OH) form of 2** ***Keto-enamine*** **(NH) form of 2**

Scheme S1 Tautomeric forms of **1** (a) and **2** (b).